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SYNTHESIS AND PROPERTIES OF RIGID-ROD
BENZOBISAZOLE POLYMERS CONTAINING
BENZOTHAZOLE PENDENT GROUPS



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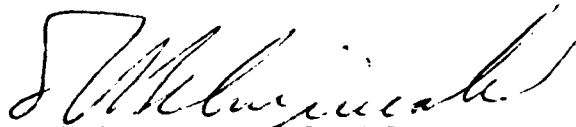
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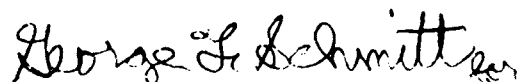


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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Nonmetallic and Composite Materials," Task No. 2303Q3, Work Unit Directive (WUD) 2303Q307, "Structural Resins." It was administered under the direction of the Materials Laboratory, Wright Research and Development Center, Air Force Systems Command, Wright-Patterson Air Force Base, OH, with Dr R. C. Evers as the Materials Laboratory Project Scientist. Co-authors were Dr Tsu-Tzu Tsai and Dr Fred E. Arnold, Materials Laboratory (WRDC/MLBP). This report covers research conducted from October 1987 to October 1988. The authors thank Dr E. G. Jones for thermogravimetric-mass spectral analysis and Dr Hoe Chuah for polymer processing work.

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SECTION 1

INTRODUCTION

In recent years there has been an increasing interest in the area of ordered polymers for their excellent tensile and modulus properties. Research efforts in our laboratory have been centered on the lyotropic rigid-rod liquid crystalline polymers. Rigid-rod polymers are defined as those materials which have a "para"-ordered geometry with only rotational degrees of freedom around the polymer axis. The class of polymers utilized in our studies has been the aromatic heterocyclic benzobisazole systems which exhibit excellent thermal and thermaloxidative stability. Modulus properties in excess of 50 MSI, with tenacity values of 500 KSI have been obtained on wet-spun fibers after heat treatment.

Synthetic research efforts on these systems more recently have been devoted to structural modifications of the rod-like polymers to promote solubility in solvents other than strong acids, as well as improve compressive properties and explore transport properties. The utilization of pendent groups along the polymer backbone has been an approach to improve the processibility by preventing the close packing of rods, thereby promoting solubility in other solvents. Pendants on extended-rod polymers have been shown [1,2] to improve solubility, but inhibit the formation of the liquid crystalline phase. Poly-p-benzamides containing bulky methyl, nitro or bromo groups affects intermolecular forces to such a large extent that lyotropic behavior was not observed, even up to concentrations as high as 45% by weight. Rigid-rod polyquinolines containing various aryether pendent groups have been reported [3] with no improvement in solubilities over the basic rigid-rod system[4]. Only limited solubility was obtained in di-m-cresyl phosphate/m-cresol.

Initial attempts in our laboratory involved pendent phenylation via the synthesis of a series of phenylated terphenyl diacids and their subsequent polymerization to benzobisoxazoles[5] and benzobisthiazoles[6]. The polymers had intrinsic viscosities in methanesulfonic acid in the range 2.5-9.3 dL/g and exhibited partial solubility (<1%) in m-cresol/strong acid mixtures. Concentrated solutions (>5%) could not be obtained in any solvent with these systems, thus prevented the insight into solution alignment of the rods. Another series of terphenyl diacids was prepared [7] which

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contained various degrees of phenoxyphenyl groups, and with these monomers polymers could not be obtained. It was initially felt that the phenoxy groups sterically hindered the carboxy functionality which prevented polycondensation. We have now determined that such nonpolar diacids were completely insoluble in the polymerization media (polyphosphoric acid) and therefore would not react.

This paper describes our work on the synthesis and polymerization of pendent benzothiazole terephthalic acids. Such diacids are quite soluble in polyphosphoric acid (PPA), which allows for the formation of high molecular weight pendent heterocyclic systems at concentrations promoting anisotropy in the polymerization solvent.

SECTION 2

EXPERIMENTAL

2.1 MONOMERS

2.1.1 2-BENZOTHAZOLE TEREPHTHALIC ACID 1 (METHOD 1)

Into a 1L three-necked flask was added 10g (4.2mmol) of 2-benzothiazole-p-xylene, 110mL of pyridine and 200mL of 5% sodium hydroxide solution. After the reaction mixture was heated to 100°C, 100g of potassium permanganate was added, with good mechanical stirring. During the addition, the temperature was maintained at 100°C and 30mL of ethanol was added to destroy any excess potassium permanganate. After stirring for another 30 min., it was filtered and the solid manganese oxide washed repeatedly with hot water. The filtrate was acidified with dilute hydrochloric acid solution to precipitate the expected acid. After recrystallization from glacial acetic acid, there was obtained 5.8g (46%), mp 287-288°C.

Anal. Calcd. for C₁₅H₉SN₂: C, 60.19; H, 3.03; N, 4.08; S, 10.70

Found: C, 60.13; H, 3.17; N, 4.63; S, 10.71

2.1.2 2-BENZOTHAZOLE-p-XYLENE

A mixture of 28.8g (22.4mmol) of 2-aminothiophenol, 33.6g (22.4mmol) of 2,5-dimethylbenzoic acid and 300g of polyphosphoric acid (PPA) was heated under a nitrogen atmosphere at 140°C for 24 hours. The reaction mixture, after cooling to 50°C, was poured into water to precipitate the compound. The precipitate was isolated by suction filtration, dissolved in chloroform and washed with dilute sodium hydroxide solution to remove residual acid. The chloroform solution was dried over magnesium sulfate, filtered, then evaporated to yield 52g (96%) of expected product. Recrystallization from anhydrous ethanol using activated charcoal provided 47g of white crystals, mp 57.5-58.0°C.

Anal. Calcd. for C₁₅H₁₃SN: C, 75.25; H, 5.47; N, 5.85

Found: C, 74.66; H, 5.54; N, 5.73

2.1.3 2-BENZOTHAIAZOLE TEREPHTHALIC ACID 1 (METHOD 2)

A solution of 5.2g (20mmole) of 2-benzothiazole-p-dicyanobenzene dissolved in 50mL of 100% phosphoric acid was slowly heated to 140 °C with stirring and maintained at that temperature for 6 hours. After the mixture was allowed to cool to room temperature, it was poured into water to precipitate the product. Recrystallization from acetic acid provided 4.7g (80%) of acid, mp 287-288 °C.

Anal. Calcd. for C₁₅H₉SN₄: C, 60.19; H, 4.08; S, 10.7

Found: C, 60.25; H, 3.98; S, 10.8

2.1.4. 2-BENZOTHAIAZOLE-p-DICYANOBNZENE

A suspension of 24g (65mmol) 2-benzothiazole-p-dibromobenzene, 13.4g (150mmol) cuprous cyanide and 150mL of N-methyl-2-pyrrolidone was heated to reflux for 24 hours. The mixture was then poured into 100mL of a 10% sodium cyanide solution to precipitate the product. The black solid was collected by filtration and chromatographed on silica gel using methylene chloride as the eluent. There was obtained 6.8g (40%) of light yellow crystals, mp 177-178 °C.

Anal. Calcd. for C₁₅H₇N₃S: C, 69.00; H, 2.70; N, 16.05

Found: C, 68.87; H, 2.84; N, 15.81

2.1.5 2-BENZOTHAIAZOLE-p-DIBROMOBNZENE

To a solvent mixture containing 300g PPA and 70g sulfolane was added 31g (11mmol) of 2,5-dibromobenzoic acid and 15g (11.3mmol) of o-aminothiophenol. The mixture was heated under a nitrogen atmosphere, at 140 °C for 24 hours. The homogeneous solution was then allowed to cool to 50 °C and poured into water which precipitated the product. The white solid that formed was collected by filtration, washed with water and air dried.

Purification of the material was carried out by chromatography on silica gel using a 50/50 mixture of hexane/methylene chloride as the eluent to afford 35g (86%) of white crystals, mp 130-131 °C.

Anal. Calcd. for C₁₃H₇Br₂NS: C, 42.3; H, 1.91; N, 3.79

Found: C, 42.5; H, 2.01; N, 3.85

2.1.6 2,5-DIBENZOTHAIAZOLE TEREPHTHALIC ACID 2

To a solution containing 200mL of a 5% potassium hydroxide and 110mL of pyridine was added 4.0g (1.0mmol) of 2,5-dibenzothiazole-p-xylene. The mechanically stirred suspension was heated to 95 °C and 27g (17mmol) of potassium permanganate was added at such a rate to maintain the temperature below 100 °C. After the addition was complete, the mixture was heated to reflux and maintained for 16 hours. The reaction mixture was cooled to

100 C and 30mL of ethanol was added to destroy excess potassium permanganate. On removal of the manganese oxide by filtration, the filtrate was extracted with methylene chloride to remove starting material and then neutralized with dilute hydrochloric acid to precipitate the expected diacid. The product was purified by redissolving in a dilute sodium hydroxide solution, treating with activated charcoal, and precipitating by concentrated hydrochloric acid to give 1.4g (30%), mp >300 C.

Anal. Calcd. for C₂₂ H₁₂ N₂ S₂ O₄: C, 61.10; H, 2.80; N, 6.48; S, 14.83.

Found: C, 61.26; H, 2.94; N, 6.03; S, 14.72.

2.1.7 2,5-DIBENZOTHAZOLE-p-XYLENE

A suspension of 10.1g (5.2mmol) of 2,5-dicarboxyl-p-xylene and 14.2g (1.1mmol) of 2-aminothiophenol in 342g of PPA was heated at 140 C under a nitrogen atmosphere for 24 hours. The mixture became a homogeneous dark green solution after 4 hours at 140 C. After cooling to 100 C, the solution was poured into 2L of water to precipitate a light green solid. The product obtained was filtered, washed with dilute (5%) sodium hydroxide solution, water and air dried. Recrystallization from methylene chloride using activated charcoal gave 16.0g (84%) of colorless crystalline product mp 209-210 C.

Anal. Calcd. for C₂₂ H₁₆ N₂ S₂: C, 70.94; H, 4.33; N, 7.52

Found: C, 71.06; H, 4.54; N, 7.01

2.2 MODEL COMPOUNDS

2.2.1 3-(2-BENZOTHAZOLYL) BENZOIC ACID

To 100mL of pyridine and 100mL of a 5% sodium hydroxide solution was added 11.2g (5.0mmol) of 3-(2-benzothiazolyl)toluene. The mixture was heated to 100 C and 50g of potassium permanganate was added over a period of 2 hours. During the addition, the temperature was maintained at 100 C and then heated at reflux overnight. To the cooled reaction mixture was added 20mL of ethanol to destroy any excess permanganate and filtered to remove solid manganese dioxide. The filtrate was acidified with diluted hydrochloric acid solution to precipitate the expected acid. After recrystallization from methanol, there was obtained 10.8g (85%) mp 266-268 C.

Anal. Calcd. for C₁₄ H₇ O₂ SN: C, 65.87; H, 3.55; N, 5.48

Found: C, 65.88; H, 3.64; N, 5.68

In an analogous oxidation procedure, the 2-isomer was obtained from 2-(2-benzothiazole) toluene in an 86% yield, mp 183-184 C.

2.2.2 2,6[2-(2-BENZOTHAZOLYL)]DIPHENYLBENZO[1,2-d:4,5-d'] BISTHIAZOLE

A suspension of 2.0g (11.0mmol) of 2,5-diamino-1,4-benzenedithiol dihydrochloride, 6.0g (23mmol) of 2-(2-benzothiazolyl)benzoic acid and 150g of PPA (84%) was heated under a nitrogen atmosphere, to 60 C and maintained at that temperature for 8 hours for complete dehydrochlorination. The reaction mixture became homogeneous and was then slowly heated to 160 C for 4 hours. After cooling to 80°C, the reaction mixture was poured into water to precipitate a yellow solid. The product was collected by filtration, washed with water and air dried to give 6.4g (96%). Recrystallization from benzene provided bright yellow crystals mp 265-266 C.

Anal. Calcd. C₃₄ H₁₈ N₄ S₄: C, 66.86; H, 2.97; N, 9.17
Found: C, 66.81; H, 3.00; N, 9.14.

Other model compounds (Table 1) were prepared by the above procedure using 2-(2-benzothiazolyl)benzoic acid or 3-(2-benzothiazolyl)benzoic acid with the appropriate amino reagent in yields (85-98%). Table 1 shows structure, purifying solvent, color and melting point as determined by differential scanning calorimetry.

2.3 POLYMERS

2.3.1 POLY[BENZO[1,2-d:4,5-d']BISTHIAZOLE-2,6-DIYL [2-(2-BENZOTHAZOLYL)-p-PHENYLENE]]

Into the bottom of a resin flask equipped with a high torque mechanical stirrer, nitrogen inlet/outlet, pressure regulator and a side opening for additions was placed 2.088g (0.85mmole) of 2,5-diamino-1,4-benzenedithiol dihydrochloride, 2.549g (0.85mmol) of 2-benzothiazole terephthalic acid and 8.78g of PPA (77% phosphorus pentoxide). The monomers were incorporated into the PPA by stirring, and the resulting mixture was then dehydrochlorinated under reduced pressure (400mm) by heating as follows: 45 C/18h; 78 C/8h; 80 C/16h; and 90 C/4h. The reaction mixture was cooled to 50°C and 6.1g of phosphorus pentoxide was added, thereby raising the final polymer concentration to 18%. Under a positive nitrogen flow, the mixture was heated at 170 C for 20 hours, then at 190°C for 4 hours. As the temperature was increased, opalescence began to appear at about 160°C. The polymer was precipitated into water, collected by suction filtration, washed with ammonium hydroxide, water, methanol, and dried under reduced pressure (0.02mm) at 110 C. An intrinsic viscosity of 19.25 dL/g was measured in methanesulfonic acid at 30°C.

Anal. Calcd. for C₂₁ H₉ N₃ S₃: C, 63.13; H, 2.27
Found: C, 62.31; H, 2.47.

**2.3.2 POLY[1,7-DIHYDROBENZO[1,2-d:4,5-d']DIIMIDAZOLE-2,6-DIYL
[2-(2-BENZOTHAZOLYL)-p-PHENYLENE]]**

The above procedure was followed except a stoichmetric quantity of 2-benzothiazole terephthalic acid and 1,2,4,5-tetraaminobenzene tetrahydrochloride was used as monomer reagents. Final polymer concentration was ten weight percent. Intrinsic viscosity as measured in methane sulfonic acid at 30°C was 7.5dL/g.

Anal. Calcd. for C₂₁ H₁₁ N₅ S: C, 69.10; H, 3.03
Found: C, 68.10; H, 3.41.

**2.3.3 POLY[BENZO[1,2-d:5,4-d']BISOXAZOLE-2,6-DIYL
[2-(2-BENZOTHAZOLYL)-p-PHENYLENE]]**

The above procedure was followed except a stoichiometric quantity of 2-benzothiazole terephthalic acid and 4,6-diaminoresorcinol dihydrochloride was used as monomer reagents. Intrinsic viscosity as measured in methane sulfonic acid at 30°C was 4.5dL/g.

Anal. Calcd. for C₂₁ H₉ O₂ N₃ S: C, 68.65; H, 2.47
Found: C, 68.53; H, 2.63.

**2.3.4 POLY[BENZO[1,2-d:4,5-d']BISTHIAZOLE-2,6-DIYL[2,5-BIS
(2-BENZOTHAZOLYL)-p-PHENYLENE]]**

The above procedure was followed except a stoichimetric quantity of 2,5-dibenzothiazole terephthalic acid 2,5-diamino-1,4 benzenedithiol dihydrochloride was used as monomer reagents. Intrinsic viscosity as measured in methane sulfonic acid at 30°C was 5.5dL/g.

Anal. Calcd. for C₂₈ H₁₂ N₄ S₄: C, 63.13; H, 2.27; N, 10.51
Found: C, 62.98; H, 2.67; N, 9.85.

**2.3.5 COPOLY[[BENZO[1,2-d:4,5-d']BISTHTAZOLE-2,6-DIYL]
(p-PHENYLENE)80%[2-(2-BENZOTHAZOLYL)-p-PHENYLENE]]20%**

A mixture of 2.85g (0.95mmole)2-benzothiazole terephthalic acid, 6.33g (3.81mmol) terephthalic acid, 11.67g (5.69mmol) 2,5-diamino-1,4-benzene-dithiol dihydrochloride and 54g PPA (77% phosphorus pentoxide) was placed in a resin flask equipped with a high torque mechanical stirrer, nitrogen inlet/outlet, and a pressure regulator. The monomers were incorporated into the PPA by stirring and the resulting mixture was then dehydrochlorinated under reduced pressure (450mm) by heating at 55°C/16h and 87°C for 16 hours. To this mixture was added, under nitrogen, 35g phosphorus pentoxide, then heated slowly to 140°C for 16 hours; and 190°C for 4 hours. The resulting liquid crystalline reaction mixture was used directly for fiber spinning. A small amount of polymer was precipitated into water, washed with ammonium hydroxide, water and methanol, and dried under reduced pressure at

1100C. An intrinsic viscosity of 16.2dL/g was measured in methanesulfonic acid at 30°C.

Anal. Calcd. for (C₁₄ H₆ N₂ S₂) 80% (C₂₁ H₉ N₃ S₃) 20% C, 63.21; H, 2.25
Found: c, 63.05; H, 2.34.

2.4 FIBER SPINNING

The polymer dopes were spun into monofilament fibers using a dry-jet wet spinning method with a 10-mil-diameter spinnerette and coagulated in distilled water. The air gap, the distance between spinnerette and the surface of the coagulant, was approximately 8 inches, and the extended wet and swollen fibers were immersed in the coagulant water bath for 24 hours. After neutralization with 3% ammonium hydroxide solution and washing with water, the fibers were tension dried at 150°C and heat treated (500-600°C) in a tube oven with 30 seconds residence time.

SECTION 3

DISCUSSION

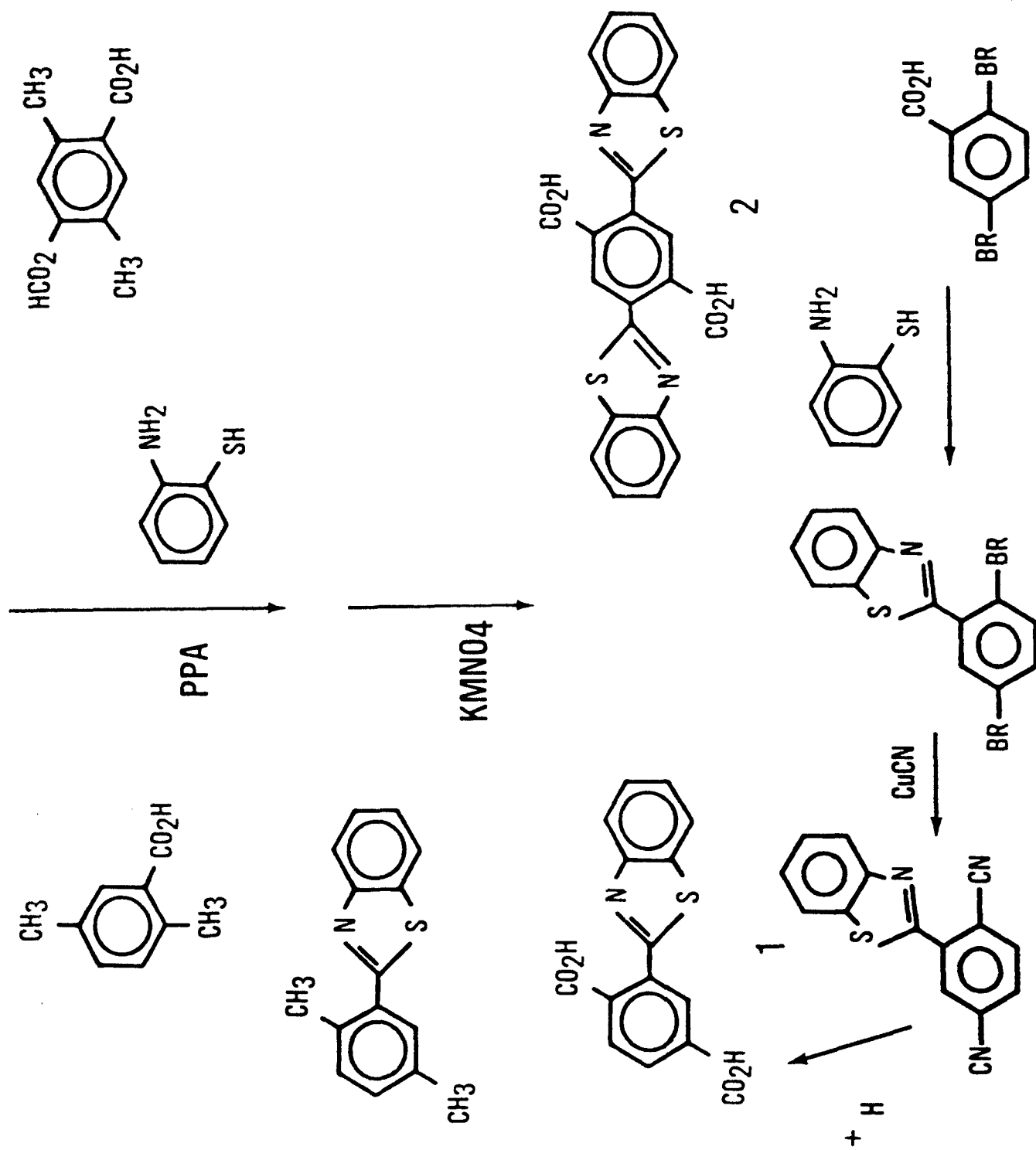
3.1 MONOMERS

The synthesis of the new monomers, 2-benzothiazole terephthalic acid (1) and 2,5-dibenzothiazole terephthalic acid (2), was carried out by the following synthetic route. Treatment of either mono or dicarboxy-p-xylenes with o-a-minothiophenol in PPA gave the benzothiazole pendent p-xylenes. Oxidation of the methyl groups with potassium permanganate in pyridine/aqueous potassium hydroxide gave the corresponding diacids after treatment with hydrochloric acid. It was found that monomer 1 could also be obtained from 2,4-dibromophenyl-2-benzothiazole by the bromo displacement reaction with cuprous cyanide followed by hydrolysis of the nitrile groups in phosphoric acid. In contrast to the insolubility of terephthalic acid, the monomers could be recrystallized from a variety of organic solvents.

SCHEME 1

3.2 MODEL COMPOUNDS

Prior to polymerization studies, benzothiazole pendent model compounds were prepared in an effort to determine if the heterocyclic group would impair reactivity by either an electronic or steric effect. The reaction of 2,5-diamino-1,4-benzenedithiol dihydrochloride, 4,6-diaminoresorcinol dihydrochloride or 1,2,4,5-tetraaminobenzene tetrahydrochloride with 2-carboxy or 3-carboxyphenyl-2-benzothiazole in PPA gave the model compounds in yields between 85-98%. Analogous to the monomer synthesis, the carboxyphenylbenzothiazoles were prepared from the condensation of



Scheme 1 (Monomer Synthesis)

ortho- or meta-toluic acids with 2-aminothiophenol in PPA followed by oxidation with potassium permanganate. Mass spectral and elemental analysis were consistent with the assigned structures. All the model compounds were crystalline, exhibiting mp. between 260-480 °C (Table I). Detailed crystal analysis of the model compounds is currently being carried out to provide accurate molecular parameters for the monomer repeat units and subsequent structural analysis of fibers.

SCHEME 2

3.3 POLYMERIZATIONS

The polymerizations of the pendent benzothiazole terephthalic acids were carried out in PPA at concentrations (10-18%) which would promote anisotropic reaction mixtures. The amine monomers used were 2,5-diamino-1,4-benzenedithiol dihydrochloride, 4,6-diaminoresorcinol dihydrochloride, and 1,2,4,5-tetraaminobenzene tetrahydrochloride to give the corresponding benzobisthiazole, benzobisoxazole, and benzobisimidazole rigid-rod polymer systems. Stoichiometric amounts of both monomers were heated in 77% PPA at 70-90°C to effect thermal dehydrochlorination of the amine monomer. This step was carried out under reduced nitrogen pressure (60mm) to facilitate removal of the hydrogen chloride. After complete dehydrochlorination phosphorus pentoxide was added under reduced pressure to provide 82-84% PPA and also compensate for the theoretical water of condensation [8]. The temperature was then raised to 170 °C and maintained at that temperature for 20 hours, and finally to 190 °C for 4 hours. The homogeneous polymer solutions normally became liquid crystalline at approximately 160 °C with an opalescent lightening of color. The liquid crystalline reaction mixtures were used directly for spinning fiber or isolated by precipitation into water and washed with water until all the phosphoric acid was completely removed. Benzobisthiazole random copolymers were also prepared in an analogous fashion except terephthalic acid and (I) were used as comonomers with 2,5-diamino-1,4-benzenedithiol dihydrochloride.

SCHEME 3

This is the first instance that a para-ordered benzobisimidazole polymer has been obtained as an anisotropic liquid crystalline solution. Previous attempts to synthesize this polymer at concentrations which would promote anisotropy always resulted in the polymer crystallizing out of solution. We found that the model compound 2,6-diphenylbenzo[1,2-d:4,5-d']bisimidazole when prepared in PPA also crystallized out of solution. A detailed crystal structure [9] of the model compound indicate four hydrogen bonded water molecules bridge the two lone electron pair nitrogen atoms on each molecule to form a ring. Since the benzimidazole ring system is a better dehydrating agent than PPA, the water of condensation can pseudo crosslink or crystallize the polymer chains. It is felt that the pendent benzothiazole groups retard the crystallizing process by preventing the close packing of chains.



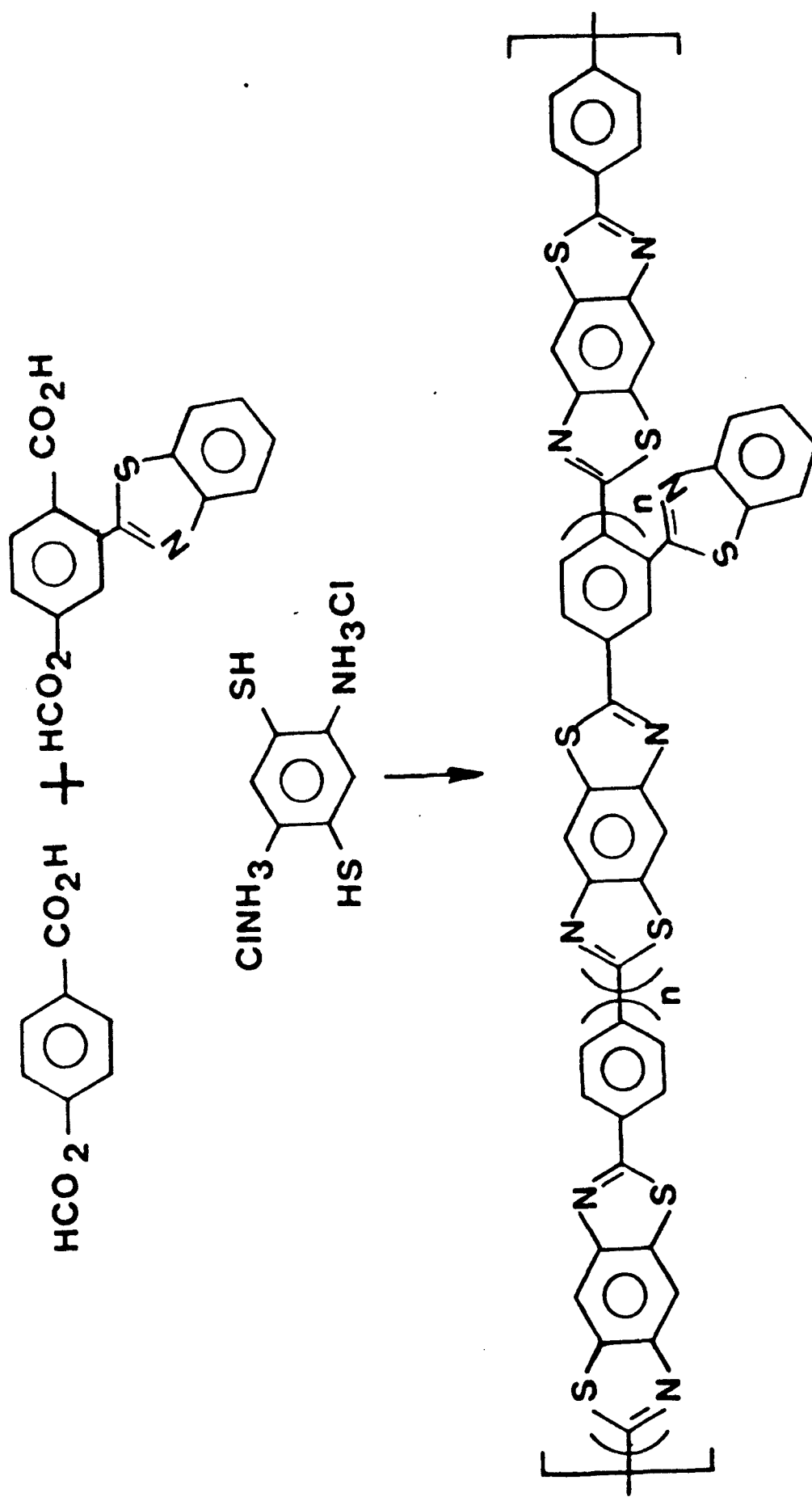
Scheme 2 (Model Compound Synthesis)

TABLE I

MODEL COMPOUNDS



HETEROCYCLIC	PENDANT BENZTHIOZOLE	PURIFYING SOLVENT	COLOR	MP
	2	BENZENE	BRIGHT YELLOW	266°C
	3	O CHLORO TOLUENE	WHITE	404°C
	2	BENZENE	WHITE	261°C
	3	TOUENE	WHITE	426°C
	2	DMAC	YELLOW	405°C
	3	DMAC	ORANGE	476°C



Scheme 3 (Copolymer Synthesis)

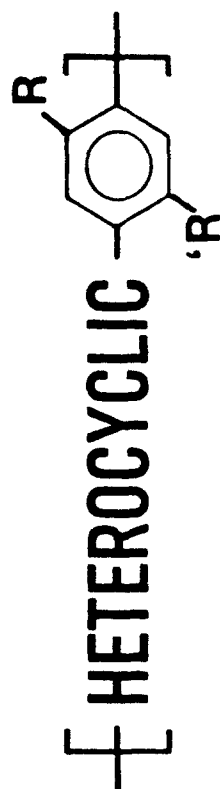
3.4 POLYMER PROPERTIES

Intrinsic viscosities (Table 2) in the range of 4-19dl/g were measured in methanesulfonic acid at 30°C. In contrast to the nonpendent rods, all the homopolymers were soluble in sulfuric acid; however, they showed no solubility in aprotic solvents. No glass transition temperatures could be found for the polymers by DSC or TMA analysis. Copolymer viscosities (Table 3) were approximately twice as high as those for the homopolymers when polymerized at the same concentrations. Although higher molecular weight materials are produced from higher concentrations, we normally polymerize below 18% to reduce the bulk viscosity for fabrication. Only one copolymer containing 20% benzothiazole pendent exhibited room temperature solubility in sulfuric acid. Other acidic or Lewis acid solvents that dissolved the polymers were PPA, methanesulfonic acid, trifluoromethanesulfonic acid, antimony trichloride and bismuth trichloride.

Along with the beneficial aspects, structural modifications of any polymer system always results in a sacrifice of some type of physical or mechanical property. The obvious effect of utilizing pendent groups is the temperature at which the group is thermally removed from the backbone chain. Pendent groups are not thermally stabilized by the long chain resonance of the backbone and are the primary degradation product. Thermogravimetric mass spectral analysis was performed in vacuo on the pendent benzothiazole-benzobisthiazole polymer at a heating rate of 3°C/min. The initial product of the thermal degradation was benzothiazole, initiating at 460°C and maximizing at 590°C (Fig 1). Other products resulting from main chain degradation were hydrogen sulfide at 710°C and carbon disulfide at 720°C. Previous thermal analysis [5] on the analogous phenylated system showed phenyl groups degrading at 580°C (initiating) and 600°C (maximizing).

The primary requirement for the attainment of high modulus and high tenacity properties is the fabrication from the liquid crystalline phase. In all cases, the anisotropic polymerization mixtures could be used directly in the formation of dry-jet wet-spun fibers. Monofilament fibers were obtained using a 10 mil- diameter spinnerette from PPA into distilled water. The swollen fibers were neutralized with 3% ammonium hydroxide, washed with water, tension dried at 150°C, and heat treated at 500-600°C with a 30-second residence time. Modulus values ranged between 25-30 MSI and tenacity values up to 350 KSI were obtained after thermal treatment under a nitrogen atmosphere. The best fibers were obtained from the higher molecular weight benzobisthiazole homopolymer and the benzothiazole pendent copolymers. Compressive properties of all the fibers as measured by the tensile recoil test [10] were between 50-55 KSI. Higher values, up to 125 KSI were

TABLE II. VISCOSITY DATA



STRUCTURE	R	'R	[η]
	H		19.3
— —			6.5
	H		4.5
	H		7.5

TABLE III COPOLYMER VISCOSITY DATA

% PENDANT THIAZOLE	POLYMER CONC. %	(n)
100	18	11.4
20	18	28.2
10	18	24.0
20	13	16.2

obtained using the bending beam test [11]; however, it has been shown in our laboratory [12] that the tensile recoil test is more comparable to actual testing the fiber in a composite.

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